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DEVELOPMENT OF SPUTTERED TECHNIQUES FOR THRUST CHAMBERS
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I. Introduction:

The objective of this program is to develop vacuum sputtering techniques for fabrication of inner and outer structures of high performance, long life regeneratively cooled thrust chambers. The investigation performed in this program is divided into five work tasks. The first task involves the application of an OFHC copper closeout layer to a ribbed wall cylinder to yield a cylindrical structure representative of regeneratively cooled thrust chambers. Within this task an investigation of materials to fill the grooved cylinder passages and selection of sputtering deposition parameters compatible with the filler materials will be performed. With the techniques developed two cylindrical structures will be fabricated; one will be forwarded to NASA-LeRC and the other evaluated for closeout layer bond strength and bond integrity. In the second task, fabrication and evaluation of 0.250 inch wall cylinders of sputtered OFHC Cu, Zr-Cu, Al_2O_3-Cu and SiC-Cu alloy will be performed. With the cylinders fabricated, an investigation of structure, hardness and tensile properties of each alloy will be determined. The third task will investigate sputtering laminated cylindrical structures. One cylinder will be sputtered with four layers of the same material, while the other will be sputtered with each layer of a different composition or a different hardness of the same composition. The materials for this task will be selected by NASA-LeRC from those evaluated in the second task of this program. Each cylinder will be evaluated for layer hardness, structure, bond integrity and bond strength. High strength outer structures will be evaluated in the fourth task. Three sputtered alloys, NASA IIb-11, Ti-5Al-2.5Sn and Al_2O_3-Al will be evaluated for tensile properties. Upon NASA-LeRC selection of one of these alloys, a homogenous cylindrical structure will be fabricated from the selected alloy and evaluated for tensile and burst strength. A second sputtered cylinder having wire reinforcement of the matrix alloy selected to make the homogenous cylinder will be fabricated. The fabricated cylinder will be burst tested to determine the strength advantage of wire reinforcement. The fifth task of the program will investigate techniques for refurbishment and coating the inner surface of thrust chambers. Inner surfaces of 2.6 inch internal diameter OFHC cylinders will be sputtered with OFHC copper, ZrO_2 and graded OFHC copper - ZrO_2 coatings. These will be evaluated for hardness, bond quality and bond integrity.

II. Technical Progress Summary

A. General:

During this reporting period, efforts were confined to the filler material study and deposition parameter study of Task I and the mandrel study of Task II. Ninety percent of the components necessary to revise the magnetron coater, for the efforts in Tasks II - V, are finished machined. Wrought targets of 0.1 Zr-Cu for Task II were received during this reporting period. All other target materials for Tasks II-V are still on order.

B. Task I: Integral Coolant Passage Filler Material

The work performed in this task was confined to examination of filler materials and further characterization of deposition parameters.

The filler materials examined in this reporting period were Cerrocast^R, Cerrotru^R, Sermetel^R 481 and flame-sprayed aluminum. The high shrinkage characteristics of Cerrocast^R resulted in incomplete filling of the grooves after repeated filling attempts. The casting technique being used with the low melting alloys would require extensive modification to allow for the shrinkage of the Cerrocast^R. Because of this, Cerrocast^R has been eliminated from further consideration.

Sermetel^R 481 has been eliminated because of its high porosity. Without using the high temperature curing cycle (1000F), which would anneal the OFHC copper substrate, the Sermetel^R 481 is porous and contains entrapped gases that prevent acceptable vacuum levels to be obtained. Furthermore, the surface could not be densified sufficiently to yield a smooth surface.

The Cerrotru^R filler was used in three experimental runs. No filler material contamination has been observed that could be attributed to the constituents of the Cerrotru^R being removed during sputter-cleaning and re-deposited during the deposition cycle. Smearing of the filler material onto the surface of the ribs was easily removed by lightly sanding the cylinder longitudinally. Pulling of the filler away from one side of the grooves resulted in the presence of small cracks extending the length of the grooves. It is believed that these cracks are replicated by the sputtered deposit resulting in cracks in the coating. Longitudinal surface grinding was attempted as a means of preventing the formation of cracks along one side of the filler material. Although surface grinding did succeed in densifying the filler, the grinding wheel rapidly fills with metal resulting in deep grooves in the filler. Removal of the grooves by hand sanding probably removed most of advantage of the longitudinal machining techniqùe, see Run I-12. Lengthwise milling of the cylinder did not result in deep machining marks, hence hand sanding was not required. The effect of longitudinal milling on crack formation will be determined during the next reporting period.

The flame-sprayed aluminum filler was used in three of the runs performed. This material, although easy to apply, does contain some porosity which results in increased pump downtime. However, it does permit higher power levels to be used during sputter cleaning which helps to outgas and clean the surface. Furthermore, the machining of the filled cylinder results in a smooth surface because the aluminum smears easily and densifies. The ease of removal of this material makes it extremely attractive as a filler material.

In an attempt to eliminate cone formation, low deposition rates were employed in the depositions performed in this reporting period. Specific data for each deposition are given in Tables I and II and discussed individually in the following. Research grade Krypton was received during this reporting period and utilized as the sputtering media for Runs I-10 through I-12.

The micro hardness data taken on all deposits is shown in Table III. Attempts to correlate the data with deposition parameters or microstructure have not been successful. It has been observed that the cones are different in hardness than the columnar structure which may account for the scatter of some of the data. Also the thinness of the closeout layers may have affected some of these data. The coatings have been limited in thickness in order to minimize the deposition time required for each phase of the parameter study.

Run I-16 - Cerrotru^R Filler; Cylinder #3118-4, Quarter Grooved

In this experiment, the substrate was cleaned by vapor blasting approximately 90% of the cylinder and polishing the remaining 10%. The deposit adherence was poorest at the polished interface. Polishing has therefore been discontinued as a cleaning technique. The cylinder used in this experiment was re-machined and used in Run I-11.

Run I-7 - Cerrotru^R Filler, Cylinder #3118-5, Quarter Grooved

The filled cylinder was cleaned initially by vapor blasting and sputtered cleaned for 5 min (-500V at 50 ma) prior to deposition of the closeout layer. Approximately 4.9 mils of copper were deposited with the system operation in the diode magnetron mode, and approximately 1.8 mils deposited in the triode mode (no field applied). These thicknesses refer to the maximum values measured at the center of the cylinder.

No filler material contamination was observed at the interface, Figure 1, and an acceptable bond resulted. However, limited cone formation and a highly directional (columnar) structure resulted in the initial deposited layer. The outer layer, deposited in the triode mode contained fewer cones, probably as a result of the increased substrate temperature (487F) achieved during deposition.

The intermediate layer resulted from attempts to operate the system at higher power levels. Since the sputtering parameters were changed continuously during this time, no data was taken on the resultant layer.

The cracking of the coating along one side of the grooves was first detected on the coated cylinder of this run, see Figure 2. Note that the cracks predominated on the non-burred side of the grooves. First thought to be a mounting artifact, the cracks were later observed during the preliminary leaching study performed on Cylinder #3118-7 from Run I-9.

Run I-8 - Sermetel^R 481 Filler, Cylinder #3118-9, Quarter Grooved

A Sermetel^R 481 filler was troweled into the grooves, air dried, the excess filler machined off, and then vapor blasted in preparation for deposition of the closeout layer. After 48 hours, the system could not be pumped down to below 2 x 10^{-6} torr due to outgassing of the filler. Because of the outgassing characteristics, and the high temperature that would be necessary to cure the filler (1000F), Sermetel 481 was eliminated as a candidate filler material.

Run I-9 - Flame-Sprayed Aluminum; Cylinder #3118-7, Quarter Grooved

The use of flame-sprayed aluminum as a filler material permitted higher power levels during sputter-cleaning and deposition. Though the porosity of the filler resulted in a longer time to reach the 5 x 10^{-8} torr background pressure standard in the procedure, the aluminum can be subjected to higher temperatures during sputter cleaning and coating without the risk of melting or evaporation.

The excess aluminum was removed by machining circumferentially as had been done for the Cerro-alloys. The smeared material had to be hand sanded with 120 grit to clean the tops of the rips prior to vapor blasting.

The somewhat equiaxed structure shown in Figure 3 might have been a result of the continuous change in deposition parameters required to prevent arcing. The unstable discharge has been attributed to a tilted target occurring in re-assembly. Note the cleanliness of the interface, indicating that the porosity of the flame-sprayed aluminum did not result in significant contamination from what could be considered virtual leaks.

A portion of this cylinder was placed in an 11.0 molar NaOH solution to remove the aluminum. A minimum removal rate of 0.25 inch per hour was achieved. During the leaching, it was noted that bubbling was occurring along one side of many of the grooves. The leaching rate was more rapid in these grooves. This has been attributed to the presence of cracks heretofore thought to be the result of mounting technique.

The leaching study will be continued during the next reporting period in order to optimize the rate of removal of the aluminum filler.

<u>Run I-10 - Flame-Sprayed Aluminum; Cylinder #3118-8, Quarter Grooved</u>

In this run, the deposition parameters were effectively the same as in Run I-9 with the exception of a higher substrate bias. Krypton instead of argon was used as the sputtering gas. The columnar structure that was observed, see Figure 4, was probably a result of the higher sputtering rate and substrate temperature. Whether the higher temperature or the increased bias accounted for the decrease in cone formation is not clear. Furthermore, the stability of the discharge probably contributed to the lack of large cones. Note the similarity between this structure and the outer layer of Run I-7 (Figures 1 and 4).

Run I-11 - Cerrotru^R Filler, Cylinder #3118-4, Quarter Grooved

In this experiment the substrate preparation procedure was slightly altered in an attempt to seal the cracks that result from the circumferential machining technique. Glass bead peening of the cylinder was utilized in an attempt to solve this problem. Although most of the cracking was eliminated, some cracks were still observed. The higher deposition rate over Run I-10 was a consequence of the higher target potential and lower substrate bias. Note that the maximum temperature at TC2 was lower for this run than for Run I-10 even though the deposition rate was higher. The lower bias and lower pressure probably accounted for this difference.

The structure of the coating shown in Figure 5 is similar to that for Run I-10 but contains more cones. The lower temperature depositions in general seem to contain more cones and as a result, higher temperature depositions are planned.

Run I-12 - Flame-Sprayed Aluminum; Cylinder #3118-12, Quarter Grooved

The machining procedure was again altered in an attempt to completely eliminate the cracking observed at the corners of some of the grooves. The cylinder for this experiment was surface ground longitudinally. Deep machining marks resulted from the wheel becoming filled with aluminum. Subsequent hand sanding with 120 grit and 325 grit to eliminate the machining marks probably removed any advantage gained by the longitudinal surface grinding operation. Some cracks were observed but they were less pronounced than in previous runs. A milling technique will be tried in an attempt to reduce the deep machining marks and eliminate the cracking of the deposited film.

The coating obtained contains three different structures (see Figure 6). The coating nearest to the substrate was similar to that observed in the previous run (i.e., columnar with many cones). The intermediate zone contains a very fine structure with some porosity. This structure resulted from the instabilities in the discharge that were observed during this period.

The outermost structure similarity to the innermost structure indicates that the higher deposition rate obtained had little effect on the elimination of cones.

From the results of the above runs, an adherent overlayer with a high integrity bond interface can be attained with Cerrotru^{R} or aluminum filler materials. The remainder of the deposition parameter study will be performed with these filler materials and with deposition parameters varied to eliminate cone formation and the closeout layer cracking at the corners of the passages. All indications show that cone formation at the low substrate temperatures (typically 120F to 220F) and at the bias conditions employed is not eliminated by lowering deposition rate. Higher temperature depositions will be tried in an attempt to completely eliminate the cones.

Task II: Sputtered Inner Wall Materials

Two depositions were performed in Task II using Type 6061 aluminum cylinders as mandrels. In both of these experiments, the aluminum was cleaned by vapor blasting, rinsing in de-ionized water and flushing with methanol prior to installation. The sputter cleaning was performed for 10 minutes in Run II-1 and 6 minutes in Run II-2 at a substrate potential of -500V (300 ma). Though the interfaces of both cylinders showed some contamination, the coatings were visually well bonded to the mandrel. Increased sputter cleaning time will be utilized in subsequent runs. The deposition parameters are listed in Table IV.

Run II-1, Cylinder #3118-101

In this experiment, four different sets of deposition parameters were examined. Note the large change in substrate current (from 3 to 100 ma) that was apparently due to the change in pressure. The deposit that resulted is shown in Figure 7. The columnar grains and cones of the structure are not unlike those observed in the lower temperature depositions of Run I-11 and the outer portion of Run I-7. Some contamination was observed at the interface which may have contributed to the cone formation.

Run II-2, Cylinder #3118-102

The deposition parameters for this run had to be continuously adjusted to prevent arcing caused by Teflon breakdown in an electrical feedthrough. No data was taken on the resultant coating except for coating thickness distribution and hardness.

Current Problems:

None.

Future Work:

During the next reporting period, the Task I deposition parameter study will be continued. Depositions employing higher substrate temperatures to eliminate cone formation and columnar structure will be performed. Variation of surface preparation will be continued in the effort to eliminate crack formation in the closeout layer at the rib wall. Tensile testing to determine closeout layer bond strength will begin and techniques for removal of Cerrotru^{R} and flame-sprayed aluminum will be refined in the next reporting period.

Fabrication of the modified coater will continue and target machining for Task II will be initiated.

TABLE I

Summary of Task I Cleaning Procedures

Run Number	Cylinder Number	Filler	Primary Cleaning	Sputter Cleaning Voltage	Sputter Cleaning Time	Sputter Cleaning Current	Pressure	Max. Temp.
I-6	3118-4	Cerrotru	90% of surface vapor blasted 10% of surface polished	-250V	5 min	100 ma	2.3 $\times 10^{-2}$ torr Ar	86F (TC_1)
I-7	3118-5	Cerrotru	Vapor blast	-500V	5 min	50 ma	2.7 $\times 10^{-2}$ torr Ar	117F (TC_2)
I-8	3118-9	Sermetal 481	Vapor blast		None - System would not pump down due to filler outgassing			
I-9	3118-7	Aluminum	Vapor blast	-900V -600V	1 min 5 min	300 ma 300 ma	4.1 $\times 10^{-2}$ torr Ar	354F (TC_2)
I-10	3118-8	Aluminum	Vapor blast	-700V -750V	1 min 5 min	300 ma 300 ma	2.5 $\times 10^{-2}$ torr Kr	609F (TC_2)
I-11	3118-4	Cerrotru	Glass bead peen	-700V -700V	1 min 1 min	300 ma 300 ma	2.9 $\times 10^{-2}$ torr Kr	344F (TC_2)
I-12	3118-12	Aluminum	350 grit polished followed by vapor blast	-650V* -750V	1 min 15 min	300 ma 300 ma	2.9 $\times 10^{-2}$ torr Kr	254F (TC_2)

* 5.0A coil current, 3 inch coil spacing during sputter cleaning

TABLE II

SUMMARY OF TASK I DEPOSITION PARAMETERS

Run Number	Cylinder Number	Filler	Substrate Voltage	Substrate Time	Substrate Current	Target Voltage	Target Time	Target Current	Magnetic Coils Current	Magnetic Coils Separation	Maximum Temperature TC_1	Maximum Temperature TC_2	Maximum Closeout Layer Thickness	Maximum Deposition Rate	Pressure
								Target A							
I-6	3118-4	Cerrotru	-35V	5 hrs	6 ma	-500V	5 hrs	4.0A	7.5A	3 in	155F	530F	N.D.	N.D.	1.3×10^{-2} Torr Ar
								Target B							
I-7*	3118-5	Cerrotru	-50V	4.5 hrs	45 ma	-690V	4.5 hrs	1.5A	5.0A	3 in	225F	462F	6.7mils	1.1 mil/hr	2.7×10^{-2} Torr Ar
			Ground	1.75 hrs	--	-690V	1.75 hrs	1.5A			487F	627F			
I-8	3118-9	Sermetel 481	No deposition-system would not pump down due to filler outgassing												
I-9	3118-7	Aluminum	-200V	4.5 hrs	140 ma	-700V	4.5 hrs	1.2A	5.0A (1 hr)	3 in	151F	182F	5.6 mils	1.1 mil/hr	4.0×10^{-2} Torr Ar 5.4×10^{-2} Torr Ar
			-100V	.75 hrs	140 ma	-700V	.75 hrs	2.0A	7.0A (2.5 hrs)	3 in	178F	196F			
									7.5A (1.75 hrs)						
I-10	3118-8	Aluminum	-300V	5.25 hrs	250 ma	-725V	5.25 hrs	1.8A	5.0A	3 in	124F	401F	6.8 mils	1.3 mil/hr	3.4×10^{-2} Torr Kr
I-11	3118-4	Cerrotru	-250V	6.0 hrs	215 ma	-800V	6.0 hrs	1.9A	5.0A	3 in	169F	263F	9.5 mils	1.6 mil/hr	2.9×10^{-2} Torr Kr
								Target C							
I-12**	3118-12	Aluminum	-250V	4.0 hrs	175 ma	-850V -1000V	3.0hrs 1.0 hr	2.0A 0.8A	7.0A 7.0A	1.5 in 3.0 in	231F 192F	198F 162F	5.0 mils	1.25 mil/hr	4.2×10^{-2} Torr Kr

* Operated in triode mode for last 1.75 hrs
** Discharge unstable during the run.

TABLE III

HARDNESS OF SPUTTERED OFHC COPPER COATINGS

Run Number	Cylinder Number	Hardness (VPN)
I-5	3118-1	128, 135, 138
I-6	3118-4	131, 145, 165
I-7	3118-5	169, 141, 141
I-9	3118-7	189, 226, 241
I-10	3118-8	169, 184, 184
I-11	3118-4	131, 145, 165
I-12	3118-12	128, 152, 226
OFHC Copper Substrate		120, 128, 138
II-1	3118-101	219, 226, 241
II-2	3118-102	141, 141, 145
Aluminum Mandrel		101, 103, 112

TABLE IV

SUMMARY OF TASK II DEPOSITION PARAMETERS

Run Number	Cylinder Number	Substrate			Target			Magnetic Coils		Maximum Temperature		Maximum Closeout Layer Thickness	Maximum Deposition Rate	Pressure
		Voltage	Time	Current	Voltage	Time	Current	Current	Separation	TC_1	TC_2			
II-1	3118-101	-50V	1.0 hr	3 ma	-900V	1.0 hr	3.0A	7.5A	3.0 in	158F	234F	12.0 mils	2.4 mil/hr	5.6×10^{-3} Torr Ar
		-50V	1.5 hr	3ma	-775V	1.5 hr	3.0A	7.5A	3.0 in					5.6×10^{-3} Torr Ar
		-100V	1.0 hr	110 ma	-770V	1.0 hr	2.0A	5.0A	3.0 in					2.7×10^{-2} Torr Ar
		-50V	1.5 hr	85ma	-850V	1.5 hr	2.5A	5.0A	3.0 in					2.7×10^{-2} Torr Ar
II-2	3118-102	-100	1.0 hr	110 ma	-820V	1.0 hr	2.0A	5.0A	3.0 in	136F	241F	3.6 mils	1.8 mil/hr	2.7×10^{-2} Torr Ar
		-200	1.0 hr	135 ma	-515V	1.0 hr	2.0A	7.5A	3.0 in					3.2×10^{-2} Torr Ar

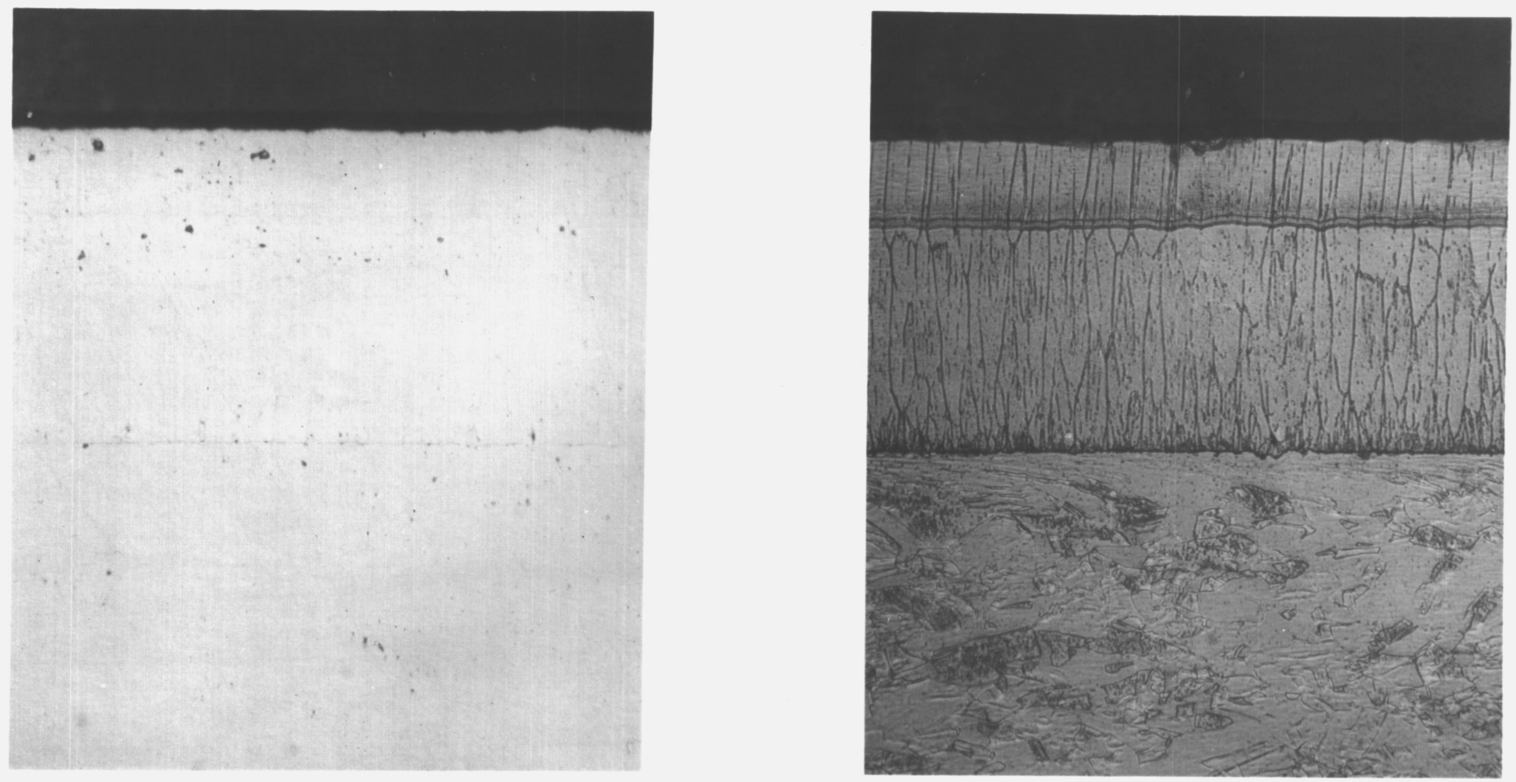

FIGURE 1: MICROSTRUCTURE OF SPUTTERED OFHC COPPER CLOSEOUT LAYER OVER CERROTRU[R] FILLED RIBBED WALL OFHC COPPER CYLINDER (#3118-5). LEFT-UNETCHED; RIGHT-ETCHED WITH 5g$FeCl_3$, 10ml HCl, 50 ml GLYCERIN, 30 ml WATER SOLUTION.

MAG: 250X

Run I-7

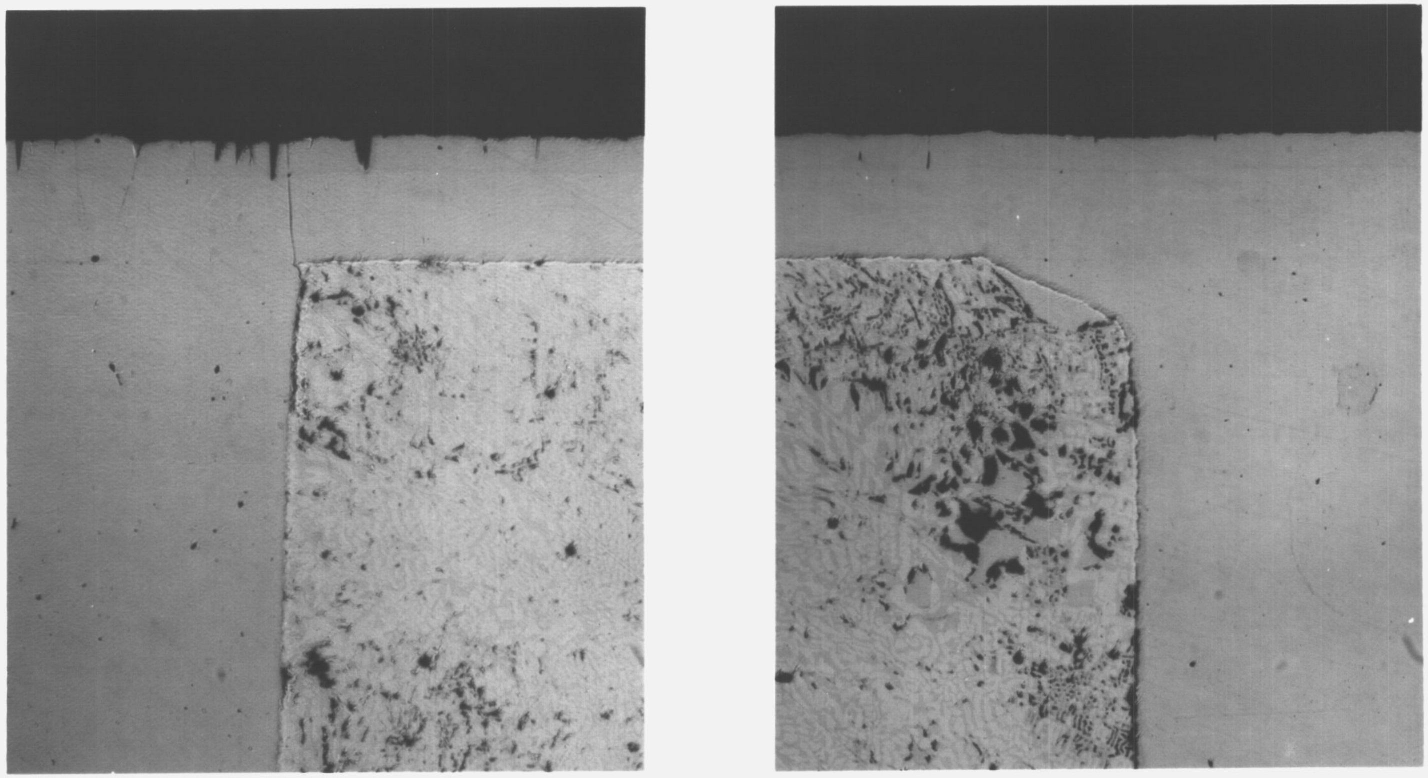

FIGURE 2: MICROSTRUCTURE OF OFHC COPPER CLOSEOUT LAYER OVER CERROTRU[R] FILLED OFHC RIBBED WALL CYLINDER (#3118-5) SHOWING CLOSEOUT LAYER CRACKING AT THE RIB WALL.

MAG: 100X UNETCHED
Run I-7

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FLORIDA RESEARCH AND DEVELOPMENT CENTER

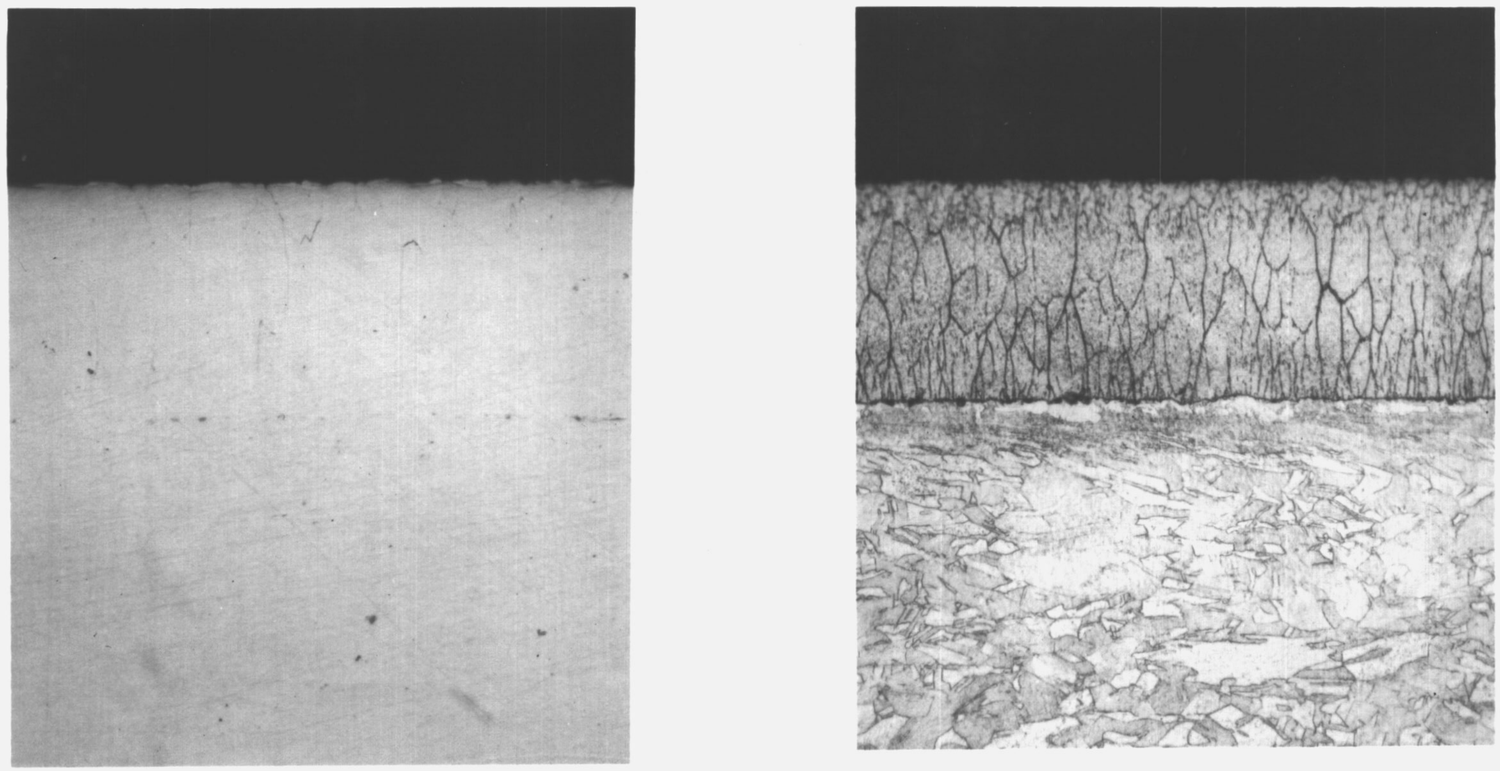
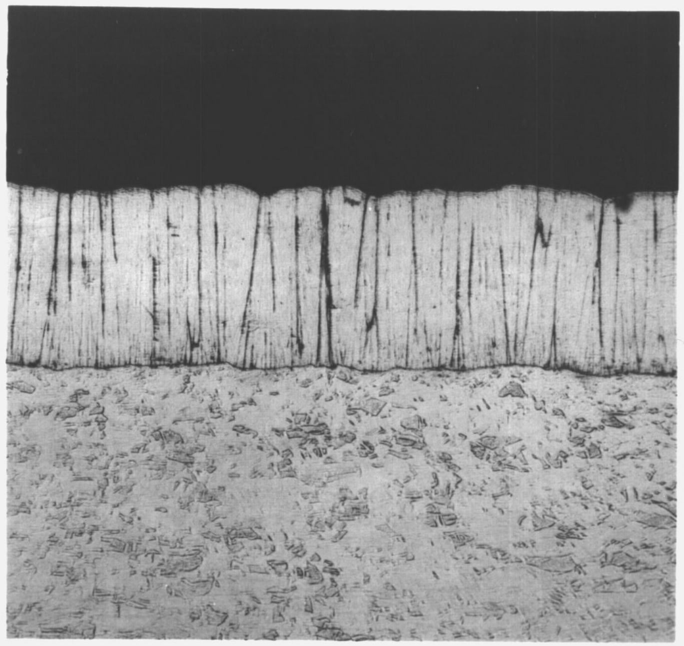


FIGURE 3: MICROSTRUCTURE OF SPUTTERED OFHC COPPER CLOSEOUT LAYER OVER FLAME SPRAYED ALUMINUM FILLED RIBBED WALL CYLINDER (#3118-7). LEFT-UNETCHED; RIGHT-ETCHED WITH 5g$FeCl_3$, 10 ml HCl, 50 ml GLYCERIN, 30 ml WATER SOLUTION.

MAG: 250X

Run I-9

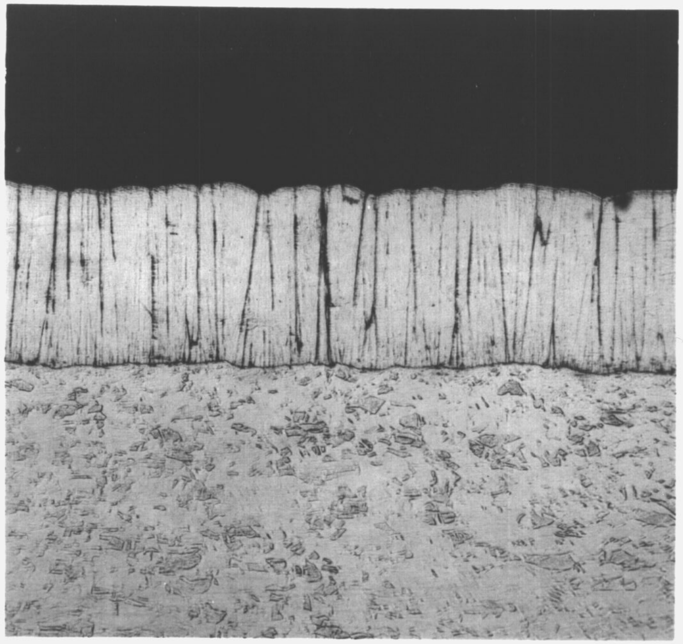


100X

250X

FIGURE 5: MICROSTRUCTURE OF OFHC COPPER CLOSEOUT LAYER OVER CERROTRU^R FILLED OFHC RIBBED WALL CYLINDER (#3118-4). ETCHANT: 5g$FeCl_3$, 10 ml HCl, 50 ml GLYCERIN, 30 ml WATER.

Run I-11



100X

250X

FIGURE 5: MICROSTRUCTURE OF OFHC COPPER CLOSEOUT LAYER OVER CERROTRU[R] FILLED OFHC RIBBED WALL CYLINDER (#3118-4). ETCHANT: 5g$FeCl_3$, 10 ml HCl, 50 ml GLYCERIN, 30 ml WATER.

Run I-11

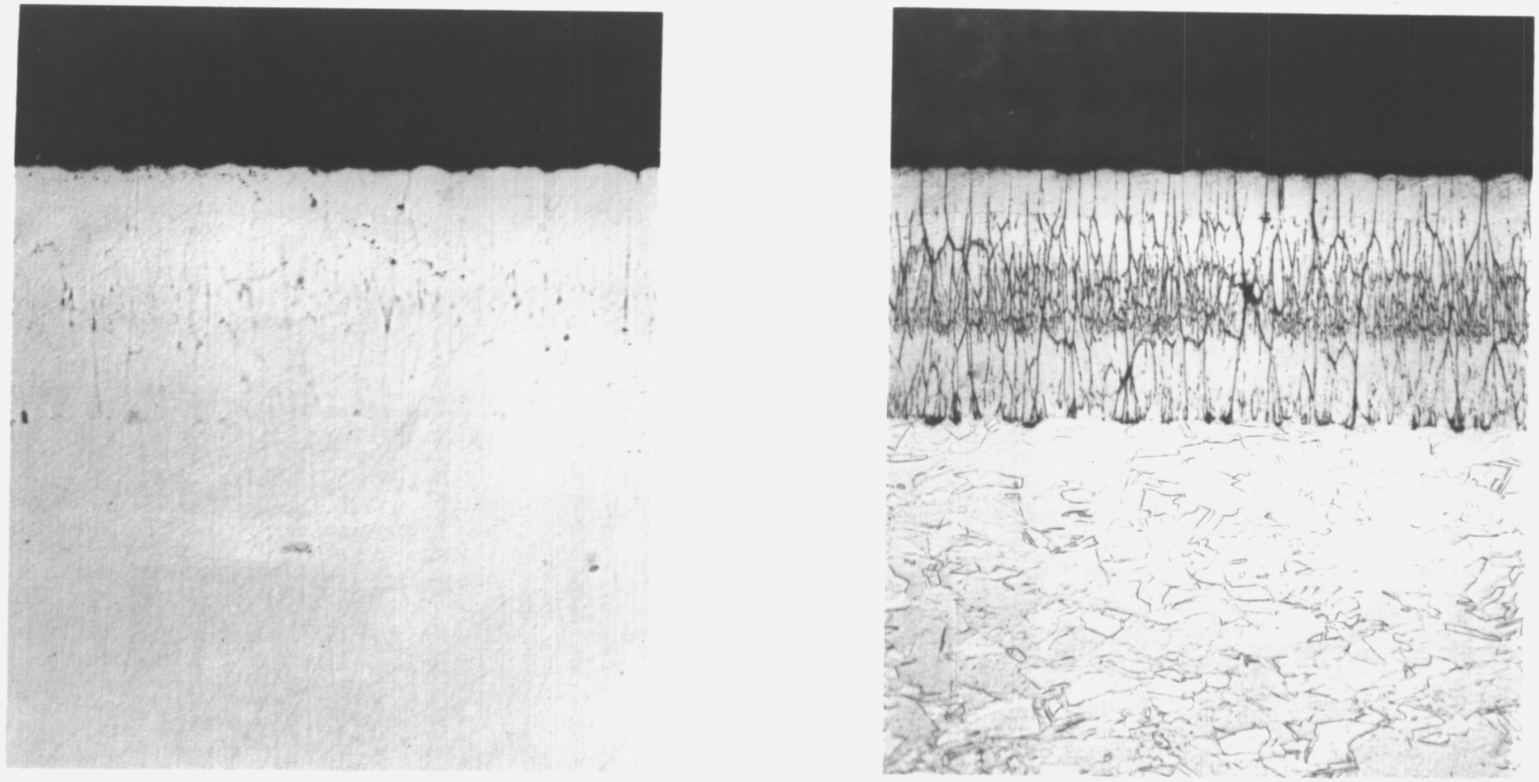
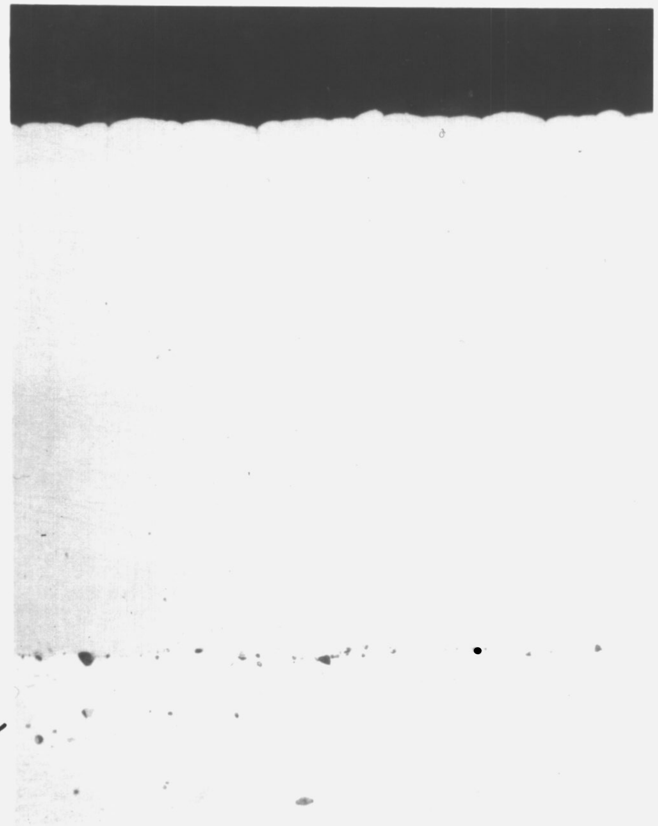


FIGURE 6: MICROSTRUCTURE OF OFHC COPPER CLOSEOUT LAYER OVER FLAME SPRAYED ALUMINUM FILLED OFHC RIBBED WALL CYLINDER (#3118-12). LEFT-UNETCHED; RIGHT-ETCHED WITH 5g$FeCl_3$, 10 ml HCl, 50 ml GLYCERIN, 30 ml WATER SOLUTION.

MAG: 250X

Run I-12



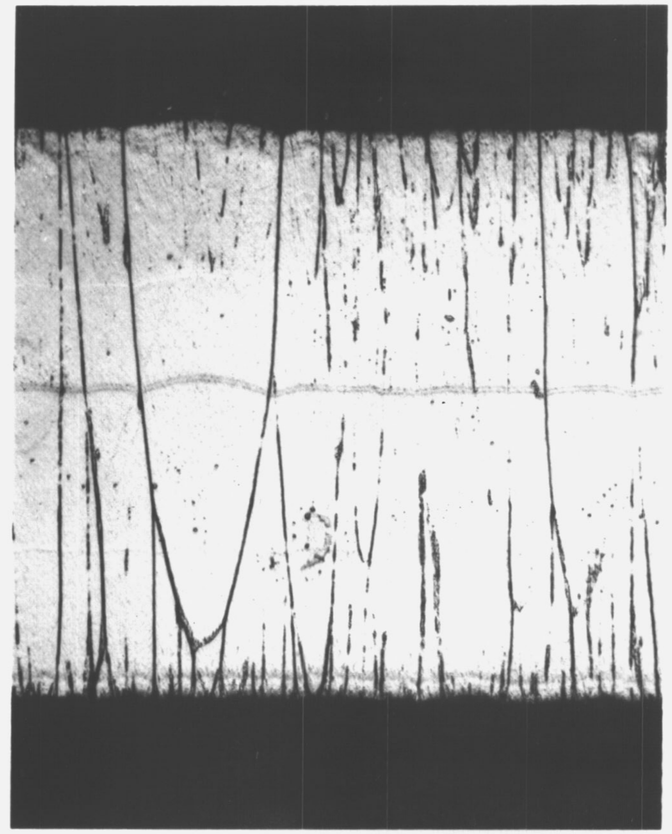


FIGURE 7: MICROSTRUCTURE OF OFHC COPPER SPUTTERED ON TYPE 6061 ALUMINUM MANDREL (#3118-101). LEFT-UNETCHED DEPOSIT ON MANDREL; RIGHT-ETCHED DEPOSIT. ETCHANT: 5g$FeCl_3$, 10 ml HCl, 50 ml GLYCERIN, 30 ml WATER.

MAG: 250X

Run II-1

PAGE ____ OF ____ PAGES

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MONTHLY CONTRACTOR FINANCIAL MANAGEMENT PERFORMANCE ANALYSIS REPORT

Form Approved
Budget Bureau No. 104-R0011

2. REPORT FOR PERIOD ENDING AND NUMBER OF OPERATING DAYS: October 31, 1973 23 WD

TO: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
CLEVELAND, OHIO 44135

FROM:

3. CONTRACT VALUE: a. COSTS $ 140 b. FEE $ 9.4

1. DESCRIPTION OF CONTRACT

a. TYPE: COST-PLUS-FIXED-FEE

b. CONTRACT NO. AND LATEST DEFINITIZED AMENDMENT NO.: NAS3-17792

4. FUND LIMITATION: $ 149.4

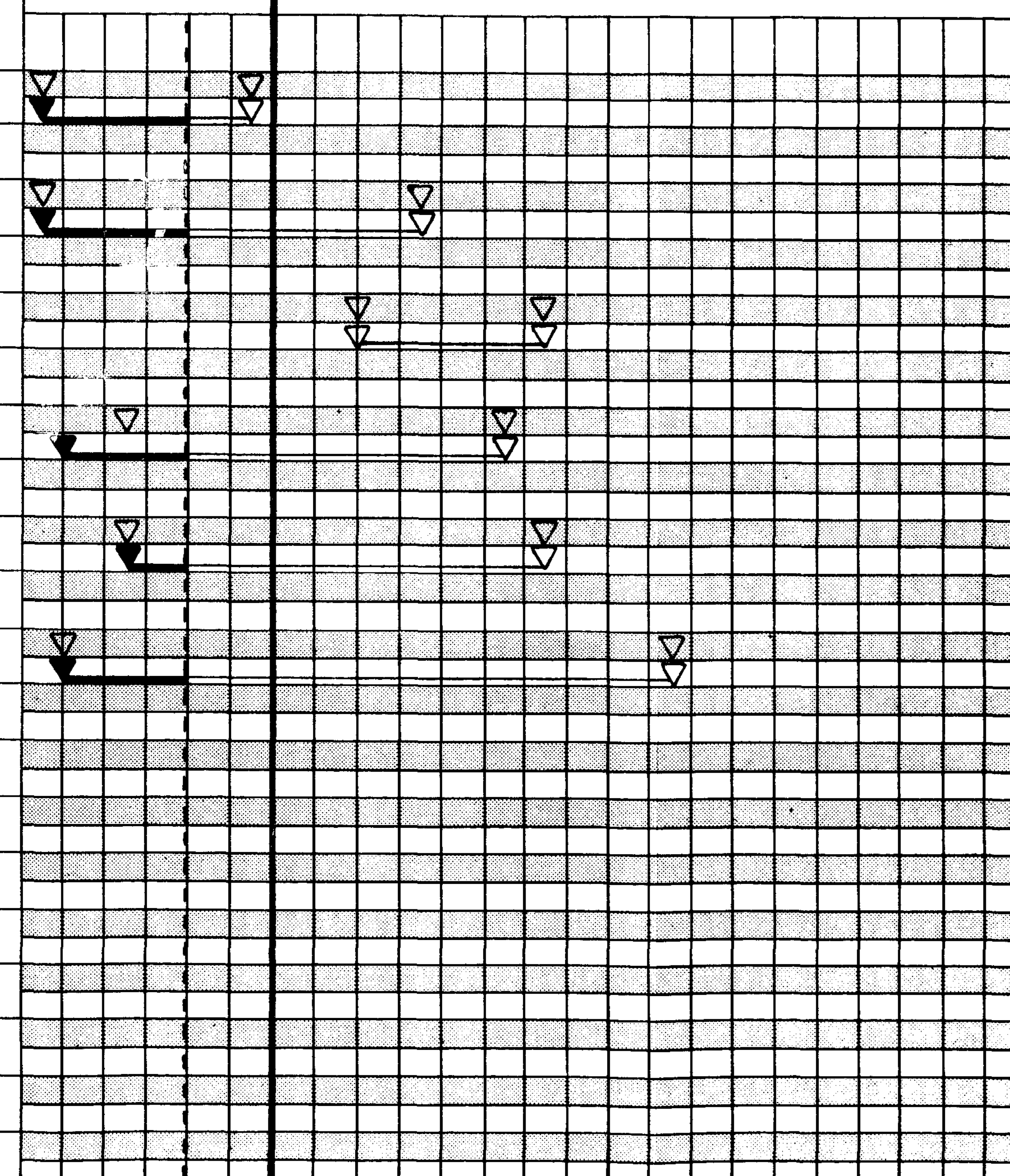
c. SCOPE OF WORK: DEVELOPMENT OF SPUTTERED TECHNIQUES FOR THRUST CHAMBERS

d. AUTH. CONTR. REP. (Signature) DATE 10/12/73

5. BILLING: a. INVOICE AMTS BILLED $ 13 b. TOTAL PYTS REC'D $ 4

6. REPORTING CATEGORY	7. PLANNED VALUE OF WORK a. SCHEDULED	7. b. ACCOMPLISHED	8. ACTUAL COSTS/HOURS	9. VARIANCE a. SCHEDULE (Col 7b - 7a)	9. b. COSTS/HOURS (Col 7b - 8)	10. CONTRACTOR'S ESTIMATED FINAL COST	11. a. SCHEDULE AND STATUS	11. b. TECH. % COMPLETED
TASK I - INTEGRAL COOLANT PASSAGE FILLER MATERIAL								50
TASK II - SPUTTERED INNER WALL MATERIAL								20
TASK III - INNER WALL GRADATION AND LAMINATION								0
TASK IV - SPUTTERED HIGH STRENGTH CYLINDERS								15
TASK V - COATED OR REFURBISHED INNER WALLS								10
TASK VI - REPORTING REQUIREMENT								

CUM. COSTS/HOURS THROUGH CURRENT PERIOD



NASA FORM 533P SEP 71

Baseline Plan Identification (Col. 7a): Revision No. ____________, Dated ____________.

NASA APPROVED SCHEDULE
CONTRACTOR'S WORKING SCHEDULE

NASA APPROVED SCHEDULE DATE 9-11-73